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Spatial distribution and controlling factors of surface water stable isotope values ($\delta^{18}O$ and $\delta^{2}H$) across Kazakhstan, Central Asia

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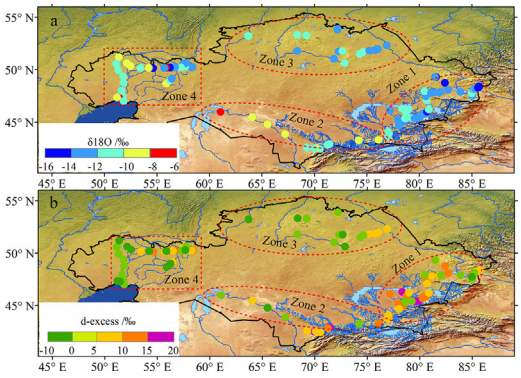
HIGHLIGHTS

- Surface water stable isotopes can be used to understand impacts of climate change.
- River water $\delta^{18}O$ exhibited a distinct spatial variability across Kazakhstan.
- The more negative isotopic values were observed in river water than lake water.
- Higher $\delta^{18}O$ values in western Kazakhstan were attributable to high evaporation.
- A gradient of river water isotopes was due to moisture from the Mediterranean.

GRAPHICAL ABSTRACT



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ABSTRACT

Climate change is expected to alter hydrological and biogeochemical processes in Central Asia (CA), and surface water stable isotope values ($\delta^{18}O$ and $\delta^{2}H$) can be used to examine these changes. Spatially extensive stable isotope data, however, are sparse, which constrains the understanding of hydrological processes in transboundary rivers across Kazakhstan. Therefore, we conducted a survey of surface water stable isotopes across the region. River and lake water isotope values exhibit spatial variability that was closely associated with isotope values of precipitation, physiographic factors, landscape characteristics, and local hydrological processes, e.g., evaporation and mixing of waters from different sources. River water was characterized by lower $\delta^{18}O$ and $\delta^{2}H$ values and higher d-excess relative to lake water, suggesting evaporative enrichment of lake water. Analysis of $\delta^{18}O$ versus $\delta^{2}H$ for rivers and lakes yielded distinct regressions, (river [RWL], $\delta^{2}H = 6.08\delta^{18}O - 16.7$, $r^2 = 0.837$, $p < 0.001$) and (lake [LWL], $\delta^{2}H = 6.23\delta^{18}O - 22.1$, $r^2 = 0.924$, $p < 0.001$). The slope and intercept of the RWL and LWL were slightly lower than the local meteoric water line [LMWL] ($\delta^{2}H = 6.96\ \delta^{18}O - 1.0$, $r^2 = 0.942$, $p < 0.001$). River water $\delta^{18}O$ showed a significant negative correlation with elevation and longitude, but not with latitude. The spatial distributions of $\delta^{18}O$ and d-excess values showed a remarkable gradient from west to east across Kazakhstan that was associated with moisture moving from the Mediterranean region to Kazakhstan. We also found generally higher $\delta^{18}O$ values and lower d-excess values in low-elevation areas because of high evaporation rate in Kazakhstan. These baseline data will be useful for documenting the effects of climate change on the hydrological cycle in Central Asia.

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1. Introduction

Central Asia (CA) is located in the hinterland of the Eurasian continent and spans 5.66×10^6 km^2, with deserts accounting for approximately one quarter of the total area. As a semi-arid and arid region, CA is highly sensitive to climate change, and increased water resource stresses has thus been experienced in the region over the past few decades (Immerzeel et al., 2010). Rising temperatures worldwide have caused substantial environmental changes that have altered the water cycle, led to extreme hydrological events, and enhanced precipitation variability (Chen et al., 2018; Karthe, 2017). CA is one of the most complex regions worldwide because of its transboundary rivers, which are shared by the post-Soviet Union states of Kazakhstan, Kyrgyzstan, Tajikistan, Turkmenistan, and Uzbekistan (Howard and Howard, 2016). The transboundary rivers are recharged primarily by precipitation and melt water, and global warming increases the complexity of the river hydrological processes (Deng and Chen, 2017; Sorg et al., 2012; Unger-Shayesteh et al., 2013). Our understanding of hydrological fluxes and water storage, and their response to climate variability, are limited in CA. It is necessary to investigate the hydrological processes of transboundary rivers in CA, given the geopolitical complexity of water resource management and human activities in the region (e.g., damming and irrigation).

Stable isotopes (δ^{18}O and δ^{2}H) in precipitation and river water are variables that provide information about hydrological processes, such as flow, evaporation, water supply, and the connectivity between aquifers within a catchment (Kendall and Coplen, 2001; Soulsby et al., 2015; Wu et al., 2019). Most isotope-based catchment studies have been conducted on small, well-instrumented catchments (Katsuyama et al., 2015; Kirchner et al., 2010; Sprenger et al., 2017; Wang et al., 2014). Few studies have used stable isotopes to investigate large river catchments (e.g., Danube River, Europe (Rank et al., 2018); Mackenzie River, Canada (Yi et al., 2010); Yangtze River, China (Wu et al., 2018)). Two of the main reasons for this are the difficulty of sampling and the complexity of hydrological processes in large catchments, making interpretation of isotopic values difficult. Large river basins are complex because of: (1) confluence of tributaries that drain sub-catchments with potentially different transit times and flow paths, (2) snow and glacier melt water inputs, (3) anthropogenic influences on evaporation because of reservoirs and irrigation, and (4) unknown and variable groundwater flows and diverse landscapes, which include lakes and wetlands with different isotope compositions (Ala-aho et al., 2018; Dutton et al., 2005; Négrel et al., 2016). All these factors result in the isotopic composition of river water potentially deviating substantially from that of local precipitation, especially in arid regions (Dutton et al., 2005; Kendall and Coplen, 2001; Timsic and Patterson, 2014). Dutton et al. (2005) found that some river segments in the USA were dominated by snowmelt and had δ^{18}O values more negative than local precipitation, whereas river water in arid regions was ^{18}O-enriched by evaporation. On the catchment scale, it was shown that stable isotope values increase downstream, i.e., with lower values in headwater regions and higher δ^{18}O values in the lower catchment (Rank et al., 2018; Rock and Mayer, 2007), mainly a consequence of the altitude effect and evaporation along the length of the river (Lachniet et al., 2016; Wu et al., 2018). Hence, there are challenges in using stable isotopes to understand hydrological processes in river catchments because complex factors control the isotopic compositions of river water at the catchment scale.

Few studies have analyzed the spatial distribution of stable isotopes in river water on a continental, or even regional scale (Brooks et al., 2014; Kendall and Coplen, 2001). Kendall and Coplen (2001) created isotope maps that show the spatial distribution of stable isotopes in surface waters across the USA. In general, the isotopic composition in precipitation is well reflected in river water, but in some areas the isotopic composition in rivers deviates substantially from that in precipitation, and requires further investigation. The global network of isotopes in rivers (GNIR) was launched by the International Atomic Energy Agency (IAEA) in 2007 (Halder et al., 2015; Vitvar et al., 2007) to investigate catchment hydrological processes. The GNIR database supplements the existing Global Network of Isotopes in Precipitation (GNIP) established in 1961 (Dansgaard, 1964). The GNIP was used initially to characterize isotope values in the atmospheric water cycle, especially moisture sources. In some regions of Central Asia, δ^{18}O and δ^{2}H variability are poorly understood, in part because of the relative lack of field observations from the GNIP or GNIR. Sparse river water samples from the Kazakhstan make it challenging to interpret the factors that control isotope variations across different landscapes. This has precluded understanding of hydrological processes within catchments, an important area of investigation in light of current and future climate change scenarios.

To fill these knowledge gaps, we collected data on the spatial variability of isotope composition in surface waters across Kazakhstan during the period between 2012 and 2015. The objectives of this study were to: (1) characterize the spatial variability of stable isotope values in river and lake waters; and (2) investigate the geographic and environmental variables that influence the isotope composition of river water. We also sought to emphasize the utility of measuring water stable isotopes in hydrological studies, in that such information can be useful for water management in light of climate change and human impacts.

2. Materials and methods

2.1. Study area

Kazakhstan is a landlocked country situated in CA. It spans a large longitudinal range (47°–88°E, 41°–55°N, Fig. 1) and has a continental climate, characterized by cold winters and hot summers. It is located on the path of westerlies that carry substantial water vapor from the North Atlantic (Karatayev et al., 2017). Frequent invasions of Siberian air masses make the area extremely cold during winter. Mean annual precipitation is 250–350 mm in northern Kazakhstan and <200 mm in the south (Fig. 2a). Mean annual temperature is 6 °C, with a minimum mean temperature of −0.2 °C and maximum mean temperature of 11.1 °C. Temperature across the region decreases with greater latitude (Fig. 2b).

Kazakhstan is distributed by vast desert landscapes and high mountainous ranges in eastern part that creates a situation for the water cycle in which glaciers play an important role, serving as the only fresh water resources. Most of the glaciers are suited in the south and east (>4000 m above sea level). On average, Kazakhstan's renewable freshwater resources amount to about 101 km^3 per year. About 56 km^3 originates in Kazakhstan, whereas the remaining ~45 km^3 originates from transboundary rivers (Irtysh, Ili, Chu, Talas, Ural and Syr Darya) that sources from the neighboring countries (Karatayev et al., 2017).

2.2. Water sampling and isotope analysis

Four regional surveys for river and lake water sampling were undertaken across multiple zones in Kazakhstan (Fig. 1) and the geographic characteristics of each zone are presented in Table S1. Total 137 river water samples and 77 lake water samples were sampled during the four surveys. The first sampling survey was carried out across eastern Kazakhstan (Zone 1) in June 2012 (n = 50 for river and n = 12 for lake). This area is part of the Ili-Balkhash Basin. Runoff originates mainly from rainfall and snow and glacier melt water in the Tianshan Mountains. The second sampling survey occurred in the lower reaches of the Syr Darya and Talas Rivers across southern Kazakhstan (Zone 2) in September 2013 (n = 15 for river and n = 7 for lake). The Syr Darya River is formed by the confluence of two large tributaries that originate from Kyrgyzstan, the Naryn River and the Kara Darya River. The third sampling survey occurred across northern Kazakhstan (Zone 3) in September 2014 (n = 15 for river and n = 57 for lake), with collecting

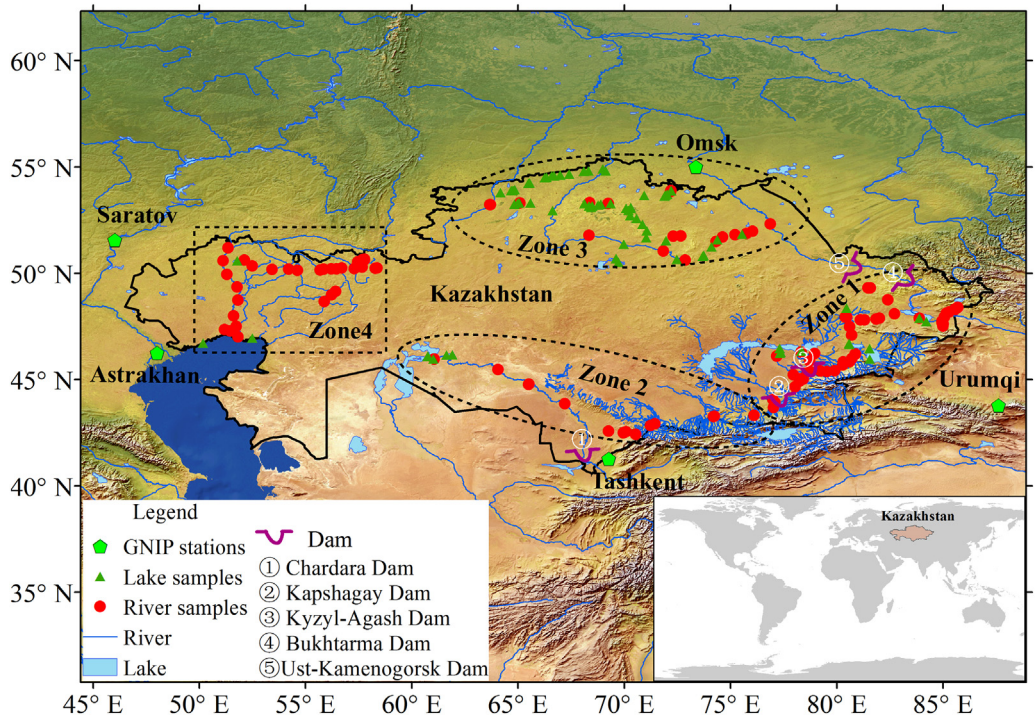

Fig. 1. Sample location map for precipitation (pentagons), river water (circles) and lake water (triangles) samples collected in different zones across Kazakhstan. Satellite–derived land cover was obtained from Natural Earth (www.naturalearthdata.com).

mainly in the catchment of the Ishim River. Large lakes and wetlands are scattered throughout this region, and show high hydrologic connectivity. The fourth sampling survey occurred across western Kazakhstan (Zone 4) in September 2015 (n = 31 for river and n = 3 for lake). Sampling sites were distributed mainly in the lower reaches of the Ural River, which originates in the Ural Mountains.

All river water samples were collected from the main stem and major tributaries (Fig. 1). Lake water samples were collected mainly

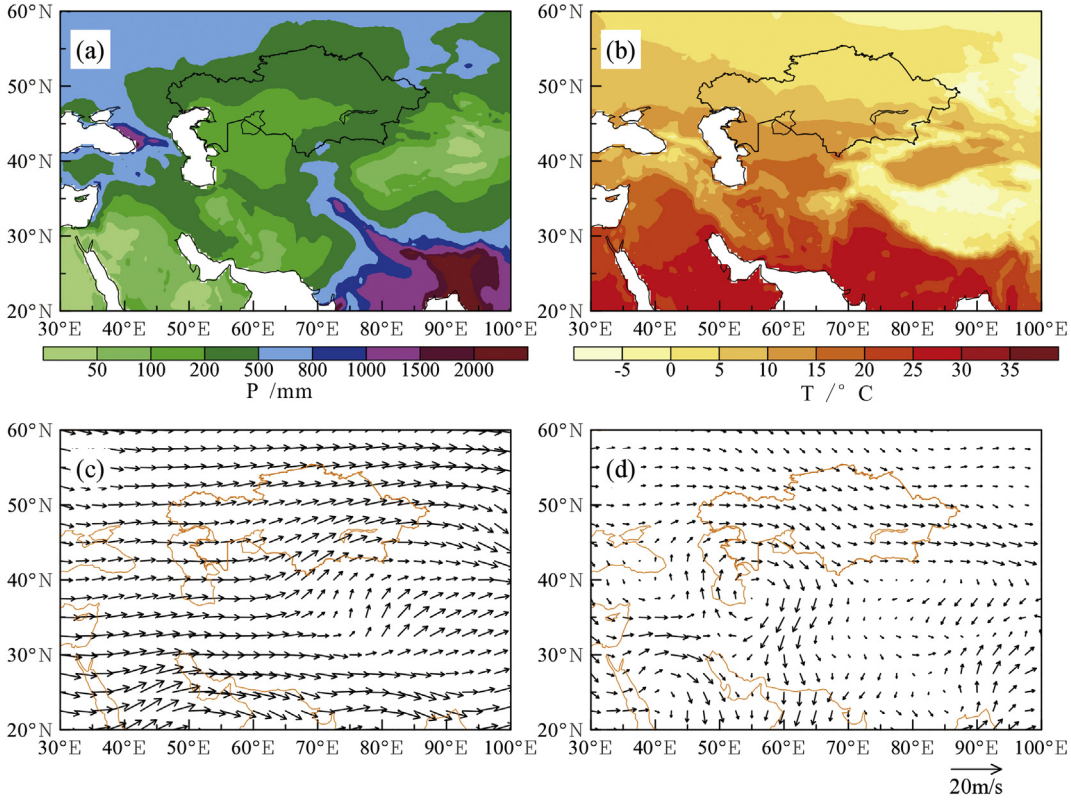

Fig. 2. Spatial distribution of annual mean precipitation amount (a), temperature (b), wind field (700 hPa) for January (c) and July (d) during the period 1960–2015.

from Zones 1 and 3 in Kazakhstan (Fig. 1). All water samples were sampled in clean, dry 30-ml bottles that were submerged to a depth of 10–15 cm in flowing waters in the rivers, or near lake shores. Sample localities coincided with road networks and trails accessible by car. Geographic data for each sample site were recorded with a portable GPS. All samples were stored in a refrigerator until analysis.

Water samples were analyzed for stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) using a Laser Absorption Water-Vapor Isotope Spectrometer (Model 908-0004, Los Gatos Research, Mountain View, CA, USA) at the State Key Laboratory of Lake Science and Environment, Chinese Academy of Sciences. Oxygen and hydrogen isotope values are expressed relative to Vienna Standard Mean Ocean Water (V-SMOW), using standard delta notation. Measurement precision values for $\delta^{2}H$ and $\delta^{18}O$ were 0.5‰ and 0.1‰, respectively, based on repeated, long-term analyses of internal laboratory standards. Deuterium excess (d-excess) was calculated to identify the influence of evaporation on the isotope compositions in river and lake water using the following equation (Dansgaard, 1964):

$$d-excess = \delta^{2}H - 8 \times \delta^{18}O \quad (1)$$

Due to the paucity of precipitation isotopes in Kazakhstan, we used precipitation isotope data from the regions neighboring Kazakhstan, including China (Urumqi), Russia (Omsk, Saratov, and Astrakhan), Uzbekistan (Tashkent), and Kyrgyzstan (Bishkek). Data were taken from the GNIP data sets (www-naweb.iaea.org/). Monthly, amount-weighted average $\delta^{18}O$ and $\delta^{2}H$ in precipitation were calculated as follows:

$$\delta\overline{P} = \frac{\sum_i^n \delta_i * P_i}{\sum_i^n P_i} \quad (2)$$

Annual mean precipitation amount, temperature, and wind field were taken from the reanalysis data sets of the NCEP-NCAR (National Centers for Environmental Prediction and National Center for Atmospheric Research, USA), for the period 1960–2015. The NCEP/NCAR data sets contain monthly-averaged wind speed, precipitation amount and temperature reanalysis data, with a spatial precision of 2.5° longitude-latitude grids (available at http://www.cdc.noaa.gov/cdc/reanalysis/). These procedures help identify changes in the source regions of precipitation over the study area.

2.3. Statistical analysis

Linear regression was used to assess relationships between geographical variables (e.g., latitude, longitude, and elevation) and isotopic compositions. The correlation coefficients and test of significance were analyzed by Pearson's method and two tailed *t*-tests, respectively. All statistical analyses were conducted using SPSS v.19.0 (SPSS Inc., Chicago, IL).

3. Results

3.1. Characterization of water stable isotopes ($\delta^{18}O$, $\delta^{2}H$, and d-excess) in rivers and lakes

River water $\delta^{18}O$ values ranged from −16.1‰ to −7.1‰, with an arithmetic mean of −11.8‰, whereas $\delta^{2}H$ values ranged from −123.5‰ to −56.8‰, with an arithmetic mean of −88.2‰. By contrast, there were remarkably higher $\delta^{18}O$ and $\delta^{2}H$ values in lake water. The $\delta^{18}O$ values varied from −10.7‰ to 2.4‰, with a mean of −4.8‰, and $\delta^{2}H$ values ranged from −90.1‰ to −9.2‰, with an arithmetic mean of −51.9‰ (Table 1). There was remarkable spatial variability of $\delta^{18}O$ values in river and lake waters across Kazakhstan (Table 1, Figs. 3a and 4a). River water $\delta^{18}O$ values showed a decreasing trend from east to west across Kazakhstan (Fig. 3a). Statistical analysis of $\delta^{18}O$ and $\delta^{2}H$ values showed that the lowest $\delta^{18}O$ and $\delta^{2}H$ values of river waters (mean $\delta^{18}O = -9.7$‰ and mean $\delta^{2}H = -69.8$‰) were found in Zone 1 (Zone 2 > Zone 4 > Zone 3 > Zone 1, Table 1). Similar to river waters, lake water $\delta^{18}O$ values also exhibited remarkable spatial variability across Kazakhstan, showing highest $\delta^{18}O$ values in west Kazakhstan (Zone 4) and lowest $\delta^{18}O$ values scattered across east Kazakhstan (Zone 1) (Fig. 4a). Highest mean $\delta^{18}O$ and $\delta^{2}H$ values of lake water ($\delta^{18}O$: 0.2‰ and $\delta^{2}H$: −13.9‰) were observed in Zone 4, followed by Zone 2, Zone 1, and Zone 3 (Table 1).

River and lake water *d*-excess values displayed a great range and spatial heterogeneity across Kazakhstan (Table 1). River water varied from −9.8‰ to 19.9‰, with an arithmetic mean of 5.9‰. Although river water from most sites in Zones 1 and 2 along the Tianshan Mountains had d-excess values >5‰, several sites had d-excess values in river water <0‰ (Fig. 3b and Table 1). The west-east gradient of river water *d*-excess was Zone 1 > Zone 2 > Zone 3 > Zone 4 (Fig. 3b and Table 1). In contrast, lake water *d*-excess values fluctuated between −38.6‰ and 2.7‰, with an arithmetic mean of −13.6‰ (Fig. 4b and Table 1). The majority (98.7%) of lake water *d*-excess values were < 0‰ except at one site in Zone 1 (d-excess = 2.72‰). The spatial trend of mean d-excess was in the order Zone 1 > Zone 2 = Zone 3 > Zone 4 (Table 1).

Correlations between $\delta^{18}O$ values and elevation, latitude and longitude were used to test the influence of these geographic variables on the isotope values. Significant negative correlations were found between $\delta^{18}O$ values and elevation ($r = -0.421$, $p < 0.001$, Fig. 5a) and $\delta^{18}O$ values and longitude ($r = -0.468$, $p < 0.001$, Fig. 5b) for river water. Latitude and $\delta^{18}O$ showed a weak negative correlation that was not significant at $p < 0.05$ ($p < 0.1$, Fig. 5c). Catchments at high elevations had lower $\delta^{18}O$ values than catchments at low elevations. The $\delta^{18}O$-elevation lapse rate was −0.3‰/100 m. Catchments in

Table 1
Summary statistics for isotope compositions of river and lake waters in different zones of Kazakhstan. Values listed are the arithmetic mean, minimum (Min), maximum (Max), sample number (N), and standard error (SE) in parentheses.

	Isotopes	River				Lake			
		Mean (‰)	Min (‰)	Max (‰)	N	Mean (‰)	Min (‰)	Max (‰)	N
Zone 1	$\delta^{18}O$	−12.8 (0.19)	−16.1	−10.2	50	−5.1 (1.32)	−10.7	2.4	12
	$\delta^{2}H$	−93.2 (1.53)	−123.5	−71.2		−53.2 (7.61)	−90.1	−9.2	
	d-excess	9.05 (0.69)	−2.2	19.9		−12.1 (3.45)	−38.6	2.7	
Zone 2	$\delta^{18}O$	−9.7 (0.39)	−11. 9	−7. 1	15	−1.9 (0.55)	−3.7	0.5	7
	$\delta^{2}H$	−69.8 (2.13)	−84.7	−56.8		−29.0 (4.13)	−41.5	−9.9	
	d-excess	7.7 (1.55)	−0.2	19.9		−13.8 (1.61)	−20.8	−7.1	
Zone 3	$\delta^{18}O$	−12.0 (0.34)	−13.6	−10.6	15	−5.4 (0.24)	−8.4	−0.9	55
	$\delta^{2}H$	−91.9 (2.09)	−106.2	−67.5		−56.6 (1.46)	−81.9	−37.4	
	d-excess	2.3 (0.92)	−4.7	8.43		−13.8 (0.77)	−31.8	−5.4	
Zone 4	$\delta^{18}O$	−11.1 (0.35)	−14.1	−7.1	31	0.2 (0.81)	−1.18	1.6	3
	$\delta^{2}H$	−86.9 (1.77)	−102.1	−66.2		−13.9 (3.95)	−21.8	−9.2	
	d-excess	2.2 (1.14)	−9.8	13.1		−15.7 (3.22)	−22.1	−12.3	

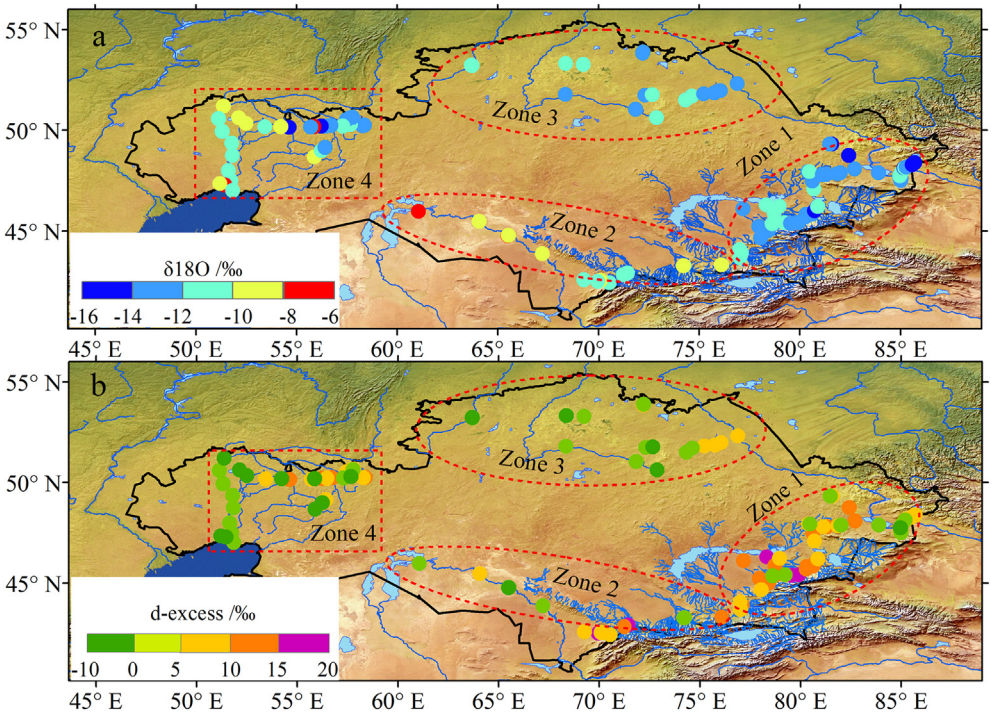

Fig. 3. Spatial distribution of $\delta^{18}O$ (a) and d-excess (b) values in river water across different zones.

eastern Kazakhstan have, on average, lower $\delta^{18}O$ values than catchments in western Kazakhstan (Table 1).

3.2. $\delta^{18}O$-$\delta^{2}H$ relationships in river and lake waters

Linear regressions between $\delta^{18}O$ and $\delta^{2}H$ for river and lake water were $\delta^{2}H = 6.08\ \delta^{18}O - 16.7$ ($r^2 = 0.837$, n = 114, $p < 0.001$) and $\delta^{2}H = 6.23\ \delta^{18}O - 22.1$ ($r^2 = 0.924$, n = 78, $p < 0.001$), which were defined as the river water line (RWL) and lake water line (LWL), respectively (Fig. 6). The slope and intercept of the RWL and LWL were similar, and deviated slightly from the local meteoric water line (LMWL) of $\delta^{2}H = 6.96\ \delta^{18}O - 1.0$ ($r^2 = 0.942$, n = 249, $p < 0.001$) based on the monthly average $\delta^{18}O$ and $\delta^{2}H$ values of GNIP sites near Kazakhstan (Fig. 6). Lake water $\delta^{18}O$ and $\delta^{2}H$ values were scattered below the LMWL and most river water $\delta^{18}O$ and $\delta^{2}H$ values were distributed along the LWML, which may be associated with the contrasting water

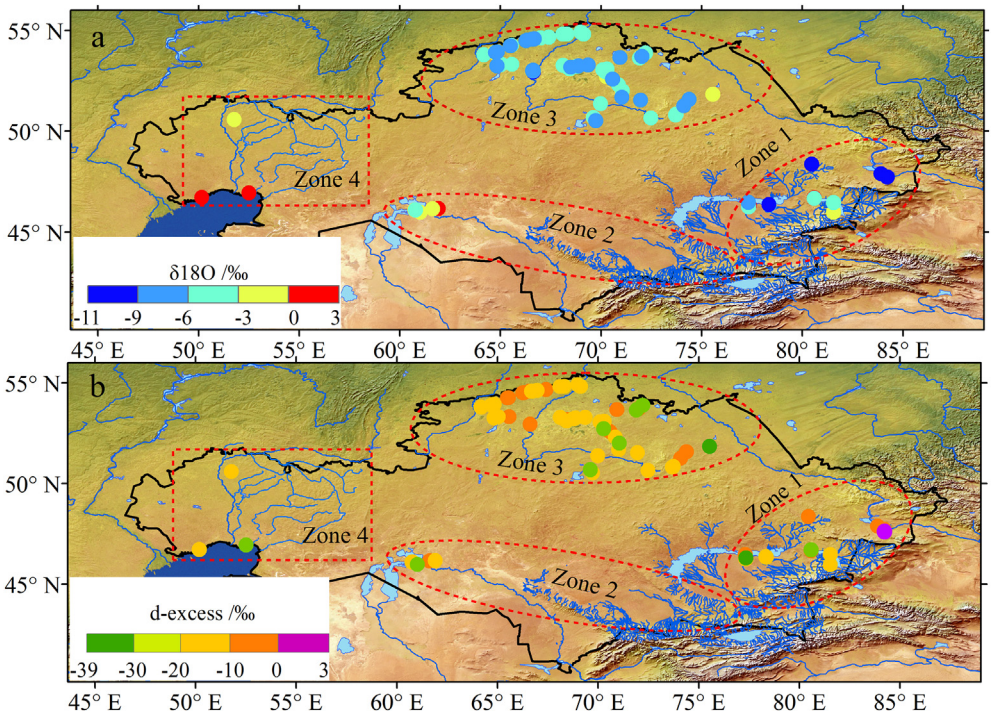

Fig. 4. Spatial distribution of $\delta^{18}O$ (a) and d-excess (b) values in lake water across different zones.

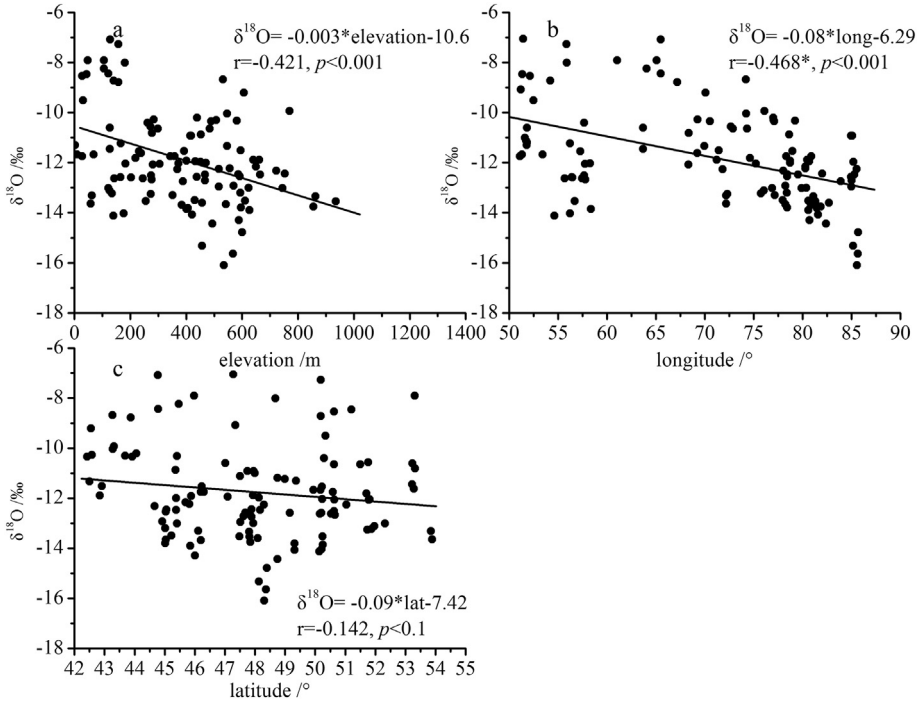

Fig. 5. Relationship of river water $\delta^{18}O$ with elevation (a), longitude (b) and latitude (c) across Kazakhstan.

sources and evaporation in lakes versus rivers. Spatially, slopes of the RWL ranged from 4.8 to 7.25 across the different zones in Kazakhstan and the highest slope (7.25) of the RWL (−0.59) was observed in Zone 1 (Table 2). In contrast, slopes of LWL varied from 4.5 to 6.99 across zones, with values ordered as follows: Zone 2 > Zone 3 > Zone 1 > Zone 4 (Table 2).

4. Discussion

4.1. Spatial distribution of $\delta^{18}O$ and $\delta^{2}H$ in surface waters

Surface waters are subject to a variety of environmental factors that influence their isotopic compositions (Kendall and Coplen, 2001; Timsic and Patterson, 2014). River water $\delta^{18}O$ and d-excess clearly display a west-east gradient across Kazakhstan (Table 1, Fig. 3), as observed for precipitation in Central Asia (Araguás-Araguás et al., 1998; Kreutz et al., 2003). Spatial patterns of river water $\delta^{18}O$ values are linked to the isotopic compositions of precipitation (Table 2). The findings conform to previous studies, showing that spatial distribution of isotopic signatures in precipitation are presented in rivers (Katsuyama et al., 2015; Kendall and Coplen, 2001). In contrast, river water *d*-excess values do not match values in local precipitation (Table 2), and display a distinct spatial pattern across Kazakhstan (Fig. 3b). The spatial pattern of river water $\delta^{18}O$ and d-excess values results from differences in evaporation, water supply, and landscape conditions across zones in the region (Fig. 7). Rivers in Zone 1 originate mainly from the Tianshan Mountains, covered by large areas of glacial with very negative isotope values ($\delta^{18}O = -16‰$ and $\delta^{2}H = -105.3‰$, Fig. 7a) (Scott et al., 2011). The lowest $\delta^{18}O$ and $\delta^{2}H$ values in river water were found in Zone 1 ($\delta^{18}O = -12.8‰$ and $\delta^{2}H = -93.2‰$, Fig. 3 and Table 1). This is a consequence of the source waters derived from snow or glacier melt in the Tianshan Mountains. Previous studies reported that snow and glacier melt in the Tianshan Mountains had lower $\delta^{18}O$ and higher d-excess values (Aizen et al., 2017; Kreutz et al., 2003) (e.g., average $\delta^{18}O = -16.0‰$ and d-excess = 23‰ from Inilcheck Glacier), and the lowest $\delta^{18}O$ values and highest d-excess values in the glacier-dominated zone (e.g., Zone 1, Figs. 3 and 7a).

Sampling sites of river water in Zone 2, in the lower reaches of the Syr Darya and Talas Rivers display higher $\delta^{18}O$ values ($\delta^{18}O = -9.7‰$ and $\delta^{2}H = -69.8‰$, Fig. 7b). This is related to the sampling sites being in the lower reaches of the Syr Darya River, where there is a large area of desert with low annual precipitation (<150 mm) and high evaporation (Kaparov, 2013; Karatayev et al., 2017). The environmental conditions are responsible for substantial isotopic enrichment along the river in Zone 2. Previous studies also reported increases in $\delta^{18}O$ values of river water with distance downstream, demonstrating the effect of continuous evaporation as water flows toward the river mouth (Reckerth et al., 2017; Yi et al., 2010). Other factors that may affect the isotopic compositions of rivers are dams (e.g., Chardara Dam) and irrigation at several points in the lower reaches of the Syr Darya River that contribute to isotopic enrichment in Zone 2. Large proportion of water withdrawals have greatly influenced the tributaries of the Amu Darya and Syr Darya, and completely altered their hydrologic regimes (Karthe, 2017). These human impacts increase water residence time, evaporation, and recharge to the groundwater (Deng and Chen, 2017).

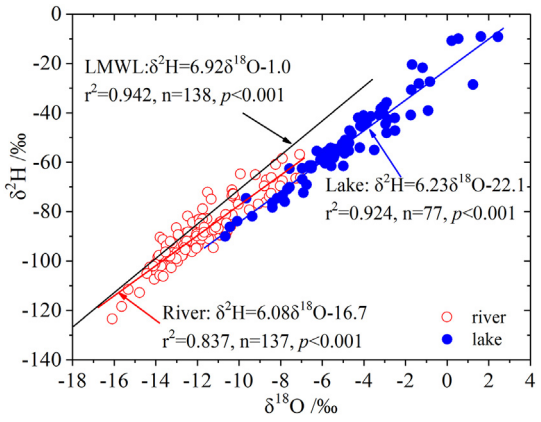

Fig. 6. Linear regression between $\delta^{18}O$ and $\delta^{2}H$ values in lake water (solid blue circles) and river water (open red circles). The local meteoric water line (LMWL) was obtained from GNIP data sets neighboring Kazakhstan.

Table 2
Regressions between $\delta^{18}O$ and $\delta^{2}H$ in river water, lake water and precipitation.

	River water	Lake water	Precipitation	$\delta^{18}O_{_p}$ (‰)	$\delta^{2}H_{_p}$ (‰)	d-excess$_{_p}$ (‰)
Zone 1	$\delta^{2}H = 7.25\,\delta^{18}O - 2.59$ ($r^2 = 0.809$, N = 50, $p < 0.001$)	$\delta^{2}H = 5.64\,\delta^{18}O - 24.2$ ($r^2 = 0.963$, N = 12, $p < 0.001$)	$\delta^{2}H = 6.98\,\delta^{18}O + 0.43$ ($r^2 = 0.934$, N = 131, $p < 0.001$)	−10.6	−72.2	12.4
Zone 2	$\delta^{2}H = 4.8\,\delta^{18}O - 22.5$ ($r^2 = 0.779$, N = 15, $p < 0.001$)	$\delta^{2}H = 6.99\,\delta^{18}O - 15.7$ ($r^2 = 0.838$, N = 7, $p < 0.01$)	$\delta^{2}H = 5.99\,\delta^{18}O - 3.39$ ($r^2 = 0.882$, N = 37, $p < 0.001$)	−7.0	−42.9	13.1
Zone 3	$\delta^{2}H = 5.92\,\delta^{18}O - 22.2$ ($r^2 = 0.917$, N = 15, $p < 0.001$)	$\delta^{2}H = 5.66\,\delta^{18}O - 26.3$ ($r^2 = 0.864$, N = 55, $p < 0.001$)	$\delta^{2}H = 7.51\,\delta^{18}O + 0.52$ ($r^2 = 0.973$, N = 8, $p < 0.001$)	−13.9	−103.6	7.4
Zone 4	$\delta^{2}H = 4.93\,\delta^{18}O - 32$ ($r^2 = 0.959$, N = 31, $p < 0.001$)	$\delta^{2}H = 4.5\,\delta^{18}O - 14.9$ ($r^2 = 0.697$, N = 3, $p < 0.1$)	$\delta^{2}H = 7.09\delta^{18}O - 1.75$ ($r^2 = 0.939$, N = 102, $p < 0.001$)	−9.5	−63.9	12.3

Notes: r^2 and N represent the regression coefficient and total number of samples, respectively. $\delta^{18}O_{_p}$, $\delta^{2}H_{_p}$ and d-excess$_{_p}$ are the monthly, amount-weighted averages for precipitation.

A previous study by Oberhänsli et al. (2009) also found high $\delta^{18}O$ values in surface water (−5.3 to 4.6‰) and groundwater (−6.86 to 3.4‰) delivered to the Aral Sea, a result of intense evaporation.

Compared with Zones 1 and 2, rivers in Zones 3 and 4 originate mainly from low-elevation mountains and flow through a vast, low-relief area with extensive lakes or wetlands (Fig. 7c, d). Rivers connected to lakes tend to have more enriched isotopic composition because of evaporation (Gibson et al., 2015). Our lake water results from Zone 3 display high $\delta^{18}O$ values and low d-excess (Fig. 4a), implying substantial evaporation of lake water. Hence, connectivity between lakes and rivers affects river water isotope compositions in Zone 3.

Rivers in Zone 4 derive from the Ural Mountains and Torgai Plateau, and are characterized by more enriched river water isotope compositions ($\delta^{18}O = -11.1‰$ and $\delta^{2}H = -86.9‰$, Table 1), compared to Zones 1 and 3. Sampling sites in the lower reaches of the Ural River display higher $\delta^{18}O$ values than those from the upper reaches of the Torgai River (Fig. 3a). This is likely related to high evaporation and landscape patterns in the lower reaches of Ural River, characterized mainly by wetlands (Fig. 7d). Wetland water is subject to high evaporation because of low flow velocity, resulting in isotopic compositions ($\delta^{18}O$ and $\delta^{2}H$) that are larger. This result is consistent with previous studies (Ala-aho et al., 2018; Yi et al., 2012), suggesting that river water mixed with the wetland water having more enriched isotopic composition than river water.

River water $\delta^{18}O$ values exhibited a significant negative relationship of both elevation and longitude, but not with altitude (Fig. 5). The terrain in the eastern Kazakhstan is, higher than that in the west. The observed lapse rate of −0.3‰/100 m for river water is similar to the global average value of −0.28‰/100 m (Poage and Chamberlain, 2001). The latitude effect, however, was not seen in river water samples from this study, because in this case, elevation increases with longitude, not latitude, and continentality effects thus are associated, in part from longitude gradients. Moreover, the longitudinal continentality effects seen in river water isotopes were attributed to westerly moisture sources from the Mediterranean (Fig. 2c, d).

Lake water isotopes exhibited remarkably higher $\delta^{18}O$ and $\delta^{2}H$ values than river water isotopes across all zones (Table 1). That is because lake water has a longer residence time and is therefore subject

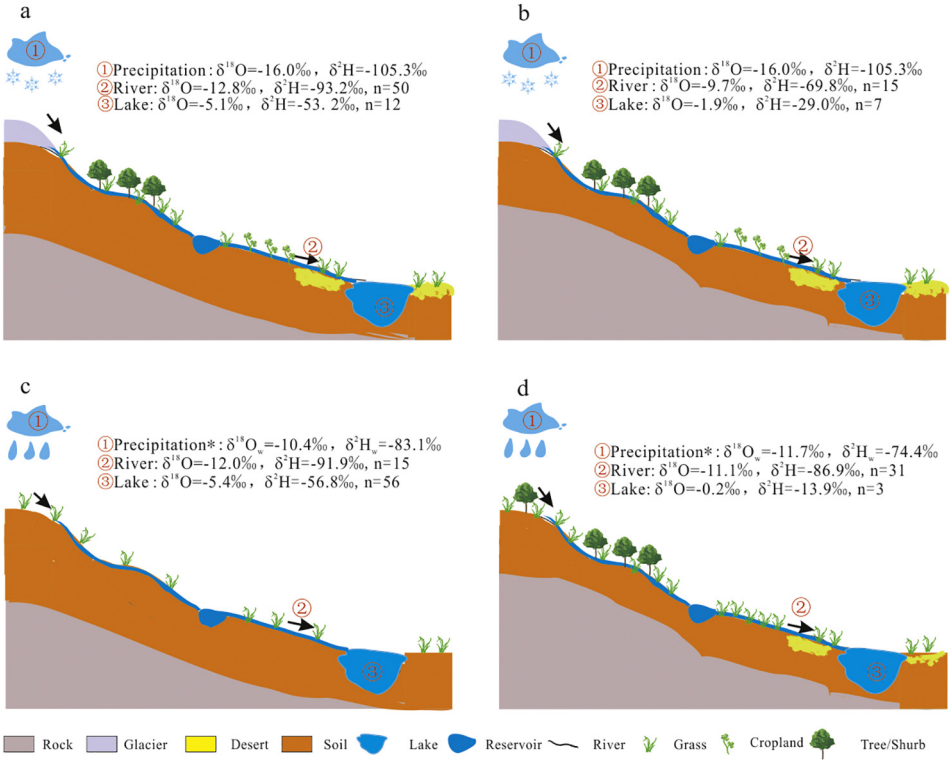

Fig. 7. Schematic illustration of landscape pattern and isotopic compositions ($\delta^{18}O$ and $\delta^{2}H$) of water types (precipitation, river, and lake) among different zones (a-d). Precipitation isotope values were obtained from glaciers in the Central Tianshan Mountains (Kreutz et al., 2003) in Zones 1 (a) and 2 (b), the Omsk in Zone 3 (c), Saratov and Astrakhan in Zone 4 (d). Symbol (*) represents the monthly, amount-weighted average of $\delta^{18}O$ and $\delta^{2}H$ in precipitation.

to greater evaporation, as shown by negative d-excess values in lake water. Lake water in Zones 2 and 4 had higher $\delta^{18}O$ and $\delta^{2}H$ values and lower d-excess compared to that in Zones 1 and 3 that is associated with differences in evaporation and recharge sources (e.g., river and precipitation) into lakes across various zones. Rivers in Zones 1 and 3 with the lowest $\delta^{18}O$ and $\delta^{2}H$ values contributed to the isotopic composition of lake water. Lake water in Zones 2 and 4, from the Caspian and Aral Seas, however, tended to display pronounced evaporative enrichment because of the arid climate and human activities in the area (Table S1). These results are consistent with previous isotope studies in the Caspian and Aral Seas (Froehlich, 2000; Oberhänsli et al., 2009).

4.2. Surface water $\delta^{18}O$-$\delta^{2}H$ relationship and d-excess

Linear regressions between $\delta^{18}O$ and $\delta^{2}H$ in precipitation and surface water are defined as the local meteoric water line (LMWL) and the surface water line (SWL), respectively, and provide a reference point to interpret stable isotope values in water samples from an area (Hughes and Crawford, 2012; Timsic and Patterson, 2014). The slope (6.96) and intercept (−1.0) of the LMWL in Kazakhstan were lower than those of the GMWL, which was similar to the Tianshan meteoric water line (slope = 6.9), derived from an ice core. The lower slope of the LMWL suggested great evaporative effect on the stable isotope composition of raindrops below the clouds. Similarly, the slope and intercept of the $\delta^{18}O$ versus $\delta^{2}H$ regression in river and lake water were slightly lower than the LMWL (Fig. 6), resulting from evaporation within the catchment, also shown by the d-excess values. This is caused by the longer residence time of lake water, increasing the greater potential for evaporation, during which lower-mass water molecules preferentially transition into the vapor phase, leading to higher $\delta^{18}O$ and lower d-excess values in residual waters (Gibson et al., 1996). Evaporation effects have been documented in river water from different climate regions, e.g., from Ireland (Diefendorf and Patterson, 2005), the North America (Kendall and Coplen, 2001), and China (Wu et al., 2017).

D-excess in precipitation is generally linked with kinetic fractionation during water evaporation (Dansgaard, 1964; Reckerth et al., 2017). Further evaporation can alter surface water *d*-excess. The mean d-excess values in river and lake was lower than the global average value of 10‰ in precipitation (Table 1). River water *d*-excess values exhibited an increasing trend across Kazakhstan (from the west to east) (Fig. 3b) that is attributed to the altitude effect and mixed water sources. Previous studies also showed that d-excess value increased with elevation, in contrast to decreasing vapor $\delta^{18}O$ (Bony et al., 2008; Liu et al., 2015). Additionally, the spatial pattern of d-excess in rivers indicates the change in moisture sources. The larger river water *d*-excess values (>15‰) from some sampling sites in west Kazakhstan suggests the impact of vapor sources from the Mediterranean and Caspian Seas (Fig. 2c, d). Earlier works showed that precipitation from neighboring the Mediterranean Sea and other inland seas is featured by higher d-excess value (Gat and Carmi, 1970). This vapor source largely contributes to the larger d-excess values in precipitation, and, thus in river water from east Kazakhstan. Kreutz et al. (2003) also found high d-excess (23‰) in an ice core from the Central Tianshan Mountains, suggesting that eastward advection of moisture from the western region (Caspian/Aral Sea) affects river water isotopes.

4.3. Broader implications for optimizing tracer-aided models of hydrology in arid environments

The spatial coverage of our stable isotope dataset is limited, but nevertheless provides isotope data that enable a better understanding of landscape patterns, local hydrological processes and water resources in rainfall- and glacier-influenced lowland areas with lakes and wetlands (Fig. 7). Local hydrological processes such as the intensity of evaporation and differences in water sources is responsible for the different spatial patterns in river and lake water isotopes across zones in Kazakhstan (Fig. 7). Such analysis aids identification of critical physiographic characteristics and hydrological processes embedded in the trace-aided hydrologic models. This study identified the dominant factors controlling surface water isotopic composition in Central Asia. Identification of key catchment processes is important to identify the potential of tracer-aided hydrologic models in arid regions (Birkel and Soulsby, 2015).

Adequate characterization of the spatial distribution of surface waters across a catchment, and evaporation from these sources, is indispensable, as these physiographic factors have substantial influence on isotopic enrichment. The ability to distribute land cover is limited in lumped models, as location is not accurately defined (Birkel et al., 2011). Hence, there is an argument in favor of using spatially distributed models. The interactions among slope, lakes and wetlands, and the enriched isotopic values at the catchment outlets remain to be worked out. Theoretical, the tracer-aided modeling studies provide a good method to study the impact of these characteristics in various environments. Obviously, catchment morphometry should be taken into consideration of other landscape elements (Tetzlaff et al., 2009). Finally, we expect that such data can be used for verifying catchment models of both flow and transport, by application of spatial variability in the isotopic compositions in surface waters in the Central Asia. This enables the consideration of the temporal patterns of flow and transport in these watershed.

5. Conclusions

We conducted a systematic regional survey of stable isotopes ($\delta^{18}O$ and $\delta^{2}H$) in river and lake water across Kazakhstan. River water was characterized by lower $\delta^{18}O$ and $\delta^{2}H$ values and higher d-excess relative to lake water, implying evaporative isotope enrichment of lake water. River water $\delta^{18}O$ and d-excess values displayed a remarkable west-east gradient across Kazakhstan that was closely associated with isotope values of precipitation, physiographic variables, landscape, and local hydrological processes (e.g., evaporation and mixing) across different zones. Lowest $\delta^{18}O$ and $\delta^{2}H$ values of river water were observed in Zone 1, where glacier and snow melt water with depleted isotopic composition dominate. The opposite was observed in Zone 2, located in the lower reaches of the Syr Darya River, where higher isotope values were attributed to greater evaporation. Lake water in Zones 2 and 4 had higher $\delta^{18}O$ and $\delta^{2}H$ values compared to values in Zones 1 and 3, differences attributable to differences in evaporation and recharge sources (e.g., river and precipitation) to lakes across zones. A strong linear relationship between $\delta^{18}O$ and $\delta^{2}H$ values in river and lake water was defined as the river water line (RWL, $\delta^{2}H = 6.08\ \delta^{18}O - 16.7$, $r^2 = 0.837$, $p < 0.001$) and lake water line (LWL, $\delta^{2}H = 6.23\ \delta^{18}O - 22.1$, $r^2 = 0.924$, $p < 0.001$). The slope and intercept of the RWL and LWL were slightly lower than those of the LMWL ($\delta^{2}H = 6.96\ \delta^{18}O - 1.0$, $r^2 = 0.942$, $p < 0.001$), resulting from evaporation in river and lake water within catchments. River water $\delta^{18}O$ showed significant negative correlations with elevation and longitude that were explained by the west-east isotope gradient across Kazakhstan. This gradient of river water isotopes was attributed to the westerly moisture sources from the Mediterranean regions. A comprehensive understanding of spatial isotope variability will permit better inferences of future changes in hydrological processes in transboundary rivers across Kazakhstan and provide basic data for studies of tracer-aided hydrologic models in Central Asia.

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